SAPPHIRE REINFORCED ALUMINA MATRIX COMPOSITES

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Abstract

Unidirectionally reinforced Al_2O_3 matrix composites have been fabricated by hot-pressing. Approximately 30 volume % of either coated or uncoated sapphire fiber was used as reinforcement. Unstabilized ZrO_2 was applied as the fiber coating. Composite mechanical behavior was analyzed both after fabrication and after additional heat treatment. The results of composite tensile tests were correlated with fiber-matrix interfacial shear strengths determined from fiber push-out tests. Substantially higher strength and greater fiber pull-out were observed for the coated fiber composites for all processing conditions studied. The coated fiber composites retained up to 95% and 87% of their as-fabricated strength when heat treated at 1400°C for 8 or 24 hours, respectively. Electron microscopy analysis of the fracture surfaces revealed extensive fiber pull-out both before and after heat treatment.

Introduction

Engine applications within the aerospace industry require materials that are capable of maintaining structural properties while exposed to both high temperatures and oxidizing environments. The extreme temperatures and environments required for these

applications can induce chemical and microstructural instabilities in a composite system which result in severe strength loss. Because of their inherent oxidation resistance and refractoriness, oxide materials are logical choices for these applications. Therefore, one system currently being studied at NASA Lewis Research Center is comprised of an alumina matrix reinforced with single crystal alumina fibers. The choice of composite materials was initially governed by fiber availability. Sapphire fibers were considered the optimum candidate in terms of microstructural stability, oxidation and creep resistance, and strength retention. Polycrystalline alumina was then chosen as the matrix material in order to avoid residual stresses that might occur as a result of a mismatch in coefficients of thermal expansion. In a brittle matrix composite such as this, proper control of the interfacial bonding is critical to the development of a strong, tough fiber reinforced material.[1-3] Therefore, an interface capable of both limiting fiber to matrix bonding and maintaining fiber strength was needed. To maintain the oxidation resistance of the entire composite system, an oxide was also selected for the interfacial coating. Because of its chemical stability in contact with alumina, unstabilized zirconia was chosen as a candidate material. It was anticipated that any phase changes that might occur during thermal cycling of the zirconia could help to weaken the interface and thereby provide a debonding path through the coating.

Ultimately, the goal of this work is to develop oxide/oxide composites for high temperature structural aerospace applications. To successfully complete this task, however, alternative single crystal fibers or fibers of a smaller diameter may be required. Therefore, the near term objective of this work, has been to demonstrate the potential of a completely oxide model system based on single crystal sapphire fibers and a porous oxide interface. To demonstrate this, composites were fabricated under various processing conditions and evaluated at room temperature. The microstructural and chemical stability

was determined by heat treating the composites at temperatures simulating those experienced during composite use and again testing the composites at room temperature. All push-out and fracture surfaces were investigated further with electron microscopy.

Experimental Procedure

Sapphire fibers, produced by Saphikon, Inc. (Milford, NH), were used as reinforcement in the oxide matrix composites. The c-axis fibers were produced by the edge-defined film-fed growth method. Fiber diameter was approximately 130 microns. Sol-gel derived ZrO_2 coatings were applied to the sapphire fibers by MSNW, Inc. (Escondido, CA). In previous studies, it was determined that porous coatings approximately 1 to 2 microns in thickness were equally or more effective in providing weak interfaces than coatings of greater thickness.[4] Therefore, porous coatings, with a uniform thickness of approximately 1.5 microns and a submicron grain size were used to provide continuous fiber coverage (fig.1). In order to avoid any possible reactions between Y_2O_3 or other stabilizing agents and the sapphire fibers, all ZrO_2 coatings were unstabilized. It was also hoped that any microcracking that might occur as a result of phase changes within the ZrO_2 could enhance crack propagation around the fibers. To determine the effects of possible interactions between the fiber and coating that might occur with thermal exposure during composite processing or use, both coated and uncoated fibers were tensile tested both before and after heat treatment. Fibers were heat-treated in air at 1200, 1300, or 1400°C for 8 hours. Extended treatments of 24 or 100 hours at 1400°C were used to confirm the stability of the coated fibers. Approximately 15 to 20 fibers were tested for each heat treatment condition. The fiber gauge length for the room temperature tests was 0.635 cm (0.25 inches).

The composite preforms were fabricated by alternating layers of unidirectionally aligned fiber mats between high purity Al_2O_3 tapes. Warm pressing of the composites at low

temperatures, before any binder burnout occurred, allowed the alumina particles to move around the fibers and penetrate the mats to produce a uniform composite microstructure. Composites were then hot pressed at either 1300° or 1400°C to reach final density. Hot pressing times of 0.5 or 2 hours were used. On the basis of preliminary mechanical testing, composites that were hot pressed at 1300°C for 0.5 hours were selected for further heat treatment in air at 1400°C for 8 or 24 hours.

Composites were tensile tested at room temperature. For each set of processing conditions, a minimum of four bars was tested. Total length of the tensile sample was 11.43 cm (4.5 inches), with a 3.81 cm (1.5 inch) gauge length between the fiber tabs. The tensile samples were tested with an Instron machine with a crosshead speed of 0.127cm/min (0.05 in/min). Strain was measured over a 25 mm length with gauges that clipped onto the sample surface. Elastic modulus was calculated from the initial linear portion of the stress vs. strain curve.

Fiber-matrix interfacial shear stress was measured with a desktop fiber push-out apparatus designed by Eldridge.[5] For these tests, the composites were cut and carefully polished to provide cross-sectional samples, approximately 0.3 to 0.4 mm thick, with parallel surfaces. From the push-out test, a load versus time curve was generated as a 100 micron punch pushed the fiber out of the matrix at a constant displacement rate. The load limit of the push-out equipment was determined by the tungsten carbide punch that was used to push the fibers out of the matrix. The upper limit of the punch was 40 N (or approximately 250 to 275 MPa for a 130 micron diameter fiber in these composite samples). Fifteen to twenty fibers were pushed out of each sample.

In addition to optical microscopy, a scanning electron microscope was used to examine the fracture surface of the tensile samples and the interfacial failure site between the fiber and matrix.

Results and Discussion

The composite microstructure, which can be observed in cross-section in Fig. 2, displayed uniform matrix density with a random fiber distribution. All matrix densities, regardless of processing conditions and heat treatment, ranged from 60 to 70% of theoretical density. The fiber volume percent was approximately 30 % for all of the unidirectionally aligned fiber composites. From the micrograph in figure 2, it is also important to note that the coating remains intact and continuous along the length of the fiber after processing. Previous work involving SnO_2 and Pt coatings in the same composite system resulted in nonuniform coatings after composite processing which led to securely bonded fibers and brittle composite behavior.[6,7]

The effects of the zirconia coatings on the on the room temperature tensile strengths of the fibers, both before and after additional heat treatment, can be seen in fig. 3. Each data point represents the average of 15 to 20 fiber tensile tests, with the error bars equal to $\pm$ one standard deviation. From these data, there was no evidence of fiber degradation caused by the fiber coating process. After exposure to temperatures of 1200 to 1400°C, both uncoated and coated fibers maintain a residual strength of 300 to 375 ksi. With further heat treatment at 1400°C for 24 or 100 hours only a slight additional strength loss was observed for the coated fibers. The residual tensile strengths measured for the coated fibers are typical of the behavior of sapphire fibers under these conditions.[6,8] Therefore the fiber coatings do not appear to be responsible for any further strength loss at temperatures that simulate those encountered during composite processing or use.

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Tensile tests of both uncoated and coated fiber reinforced composites demonstrated the effectiveness of the ZrO_2 fiber coatings. Representative stress vs. strain curves generated from these tensile tests are displayed in figure 4. For comparison, monolithic alumina hot pressed under the same conditions and with the same tapes used for the composites was also tested. As expected, the porous monolithic material display s both low strength and strain to failure. The composite reinforced with the uncoated fibers benefits from the high modulus of the fibers and yields a much higher composite modulus, however, due to excessive bonding between the fiber and matrix, the ultimate strength is still quite low. The stress strain curves for the ZrO_2 coated fiber reinforced composites reveal the influence of the interfacial coating. The curves for these composites consistently extended well beyond those of the monolithic or uncoated fiber materials. Both ultimate strength and strain to failure are increased by the weaker interface provided by the ZrO_2 coating.

The average ultimate tensile strengths of the coated and uncoated fiber reinforced composites are displayed graphically in figure 5. Each bar on this graph represents the average of 4 or more room temperature tests. Of the four sets of processing conditions studied, the lowest and least severe conditions yielded the highest strength composites. The ZrO_2 coated fiber reinforced composites processed at 1300°C for 0.5 hours possessed an average ultimate tensile strength of 421 ± 36 MPa. Uncoated fiber reinforced composites processed under the same conditions failed at a much lower strength of 130 ± 49 MPa due to strong bonding between fiber and matrix. The decrease in strength with increasing processing temperature and time is thought to be due to both increased bonding at the interface and also fiber strength loss which occurs with composite processing under pressure. The change in microstructure of the coating is responsible for both the increased bonding and the fiber strength loss. As the processing temperature and time are increased, the coating densifies and coarsens which leads to an interface that is too strong to allow failure within the coating. Also, the grain growth in the coating that

occurs during hot pressing and consolidation of the composite leads to a roughened fiber surface that mirrors the roughness of the ZrO_2 grains. This roughening of the fiber surface in addition to the coarsening of the coating leads to increased bonding at both the fiber and matrix interface. It is believed that this exaggerated roughening of the fiber surface, which has been observed and reported previously, leads to fiber strength loss.[9,10] The composite tensile fracture samples, which are seen in figure 6, display the fiber pull-out that was observed in all coated fiber composites. Although fiber pull-out decreased slightly with increasing processing temperature and time, all composites reinforced with ZrO_2 coated fibers displayed some degree of pull-out after tensile testing. As expected, the uncoated fiber composites which failure at a much lower stress and strain, behaved in a brittle manner with no fiber pull-out.

Stress vs. strain behavior of the heat-treated composites can be seen in figure 7. Only the coated fiber composites processed at 1300°C for 0.5 hours received further heat treatment and evaluation. The composites continued to fail in a non-brittle manner with little change in ultimate strength, however a significant increase in modulus was observed. This increase may be explained in part by the increase in matrix density that occurred with further thermal exposure. However, the increase in density is so slight it is unlikely that it could be responsible for the total increase in modulus (refer to Table 1). Therefore it is believed that the increase in modulus is also related to the change in microstructure of the interfacial coating. Because the coating microstructure densifies and coarsens with heat-treatment, it is believed that the change in modulus is related to this localized densification around the fibers. Although the interface becomes more rigid, the coating is still capable of limiting fiber/matrix bonding and maintaining composite strength after heat-treatment to 1400°C for 24 hours. The average ultimate tensile strengths measured for the heat-treated composites are displayed in figure 8. After heat-treatment at 1400°C for 8 or 24 hours, the coated fiber composites retained 95 or 87% of their strength, respectively. This

strength retention indicates that exposure to expected use temperatures without the application of pressure will not severely degrade the fiber and composite strengths. The heat-treated samples when tested in tension continued to display considerable fiber pull-out (fig. 9).

The interfacial shear stresses (ISS) for only the ZrO_2 coated fiber reinforced composites are displayed in figure 10. Fiber push-out tests of uncoated fiber reinforced composites were not possible due to equipment failure or excessive cracking of the matrix and fiber caused by the extremely high loads needed to shear the strong fiber/matrix bond. Each bar in this graph represents the average of 15 to 20 fibers pushed out of the matrix. With coated fibers, the as-fabricated composite yielded a relatively low ISS of 58 MPa. After exposure to 1400°C for 8 or 24 hours the ISS increased to 66 and 83 MPa, respectively. It is believed that this increase is due to the coarsening and densification of coating microstructure that was observed in the SEM.

This change in the coating microstructure can be seen in the micrographs in figures 11 and 12. Examination of the fracture surfaces from composites hot-pressed at 1300°C and then tensile tested at room temperature revealed a substantial amount of residual ZrO_2 remaining on the fibers which pulled out of the matrix (fig. 11.a). Closer inspection of the darker areas on the pulled out fiber reveal more fine grained ZrO_2 adhering to the fiber surface(fig. 11.b), thus indicating that interfacial failure can occur within the coating layer. In general, the lowest ISS was measured when interfacial failure occurred within the coating layer rather than at the coating/matrix or coating/fiber interface. There was no evidence of pitting or roughening of the fiber surface after the initial processing at 1300°C for 0.5 hours. The change in microstructure of the interfacial coating after heat treatment to 1400°C for 24 hours (fig. 12) is consistent with the increase in the interfacial shear stress. In these composites the interfacial failure occurs at either the fiber/coating

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interface or the coating/matrix interface, but not within the coating itself. The coating has coarsened considerably thus causing severe roughening of the fiber surface. Other researchers have shown that interfacial roughness has a significant influence on interfacial debonding in brittle matrix composites.[11,12] The increased coating density and grain size combined with the roughening of the fiber surface result in greater difficulty in debonding the fibers.

Conclusions

The results of this work have demonstrated that the viability of an oxide/oxide system depends on the selection of an adequate interfacial coating. Porous, unstabilized zirconia coatings led to non-brittle failure in these composites. The coating microstructure had a considerable influence on the effectiveness of the interface and the resulting composite properties. As the interfacial grain size and density increased with processing conditions, both fiber surface degradation and interfacial shear stress also increased resulting in lower fiber and composite strength. Further heat treatment at $1400^{\circ}C$ in air under ambient pressure for 24 hours produced minimal composite strength loss thus indicating the stability of the oxide/oxide system at anticipated composite processing and use temperatures. Overall, these results suggest that oxide composite systems have considerable potential for structural applications in oxidizing environments. To fully realize this potential, optimization of the matrix will be required along with further evaluation of the high temperature composite behavior.

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Composite Properties

Fiber Coating/ Treatment	Matrix Density (% TD)	Tensile Strength (MPa)	Tensile Modulus (GPa)	Strain (%)
Monolithic/ As-fabricated	63.0	57.96	59.26	0.10
No coating/ As-fabricated	60.6	129.7	187.8	0.076
No coating/ 1400C/24hr	64.1	89.23	263.5	0.033
Zirconia/ As-fabricated	61.5	421.0	158.1	0.348
Zirconia/ 1400C/8hr	62.8	402.2	232.2	0.217
Zirconia/ 1400/24hr	69.8	365.0	253.8	0.210

Table I. Room temperature properties of monolithic Al_2O_3, and ZrO_2 coated and uncoated sapphire reinforced Al_2O_3 matrix composites both as-fabricated (1300°C, 0.5 hr) and after additional heat treatment.
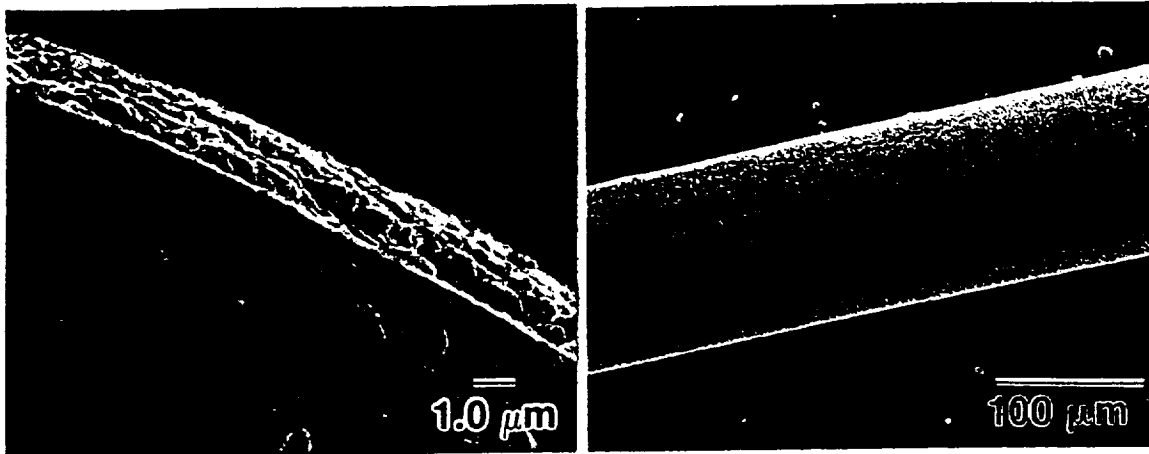
Figure 1. Sol-gel derived ZrO_2 coatings on Saphikon fibers.

Figure 2. Cross-section of hot-pressed fiber reinforced composite showing random fiber distibution and uniform matrix density.
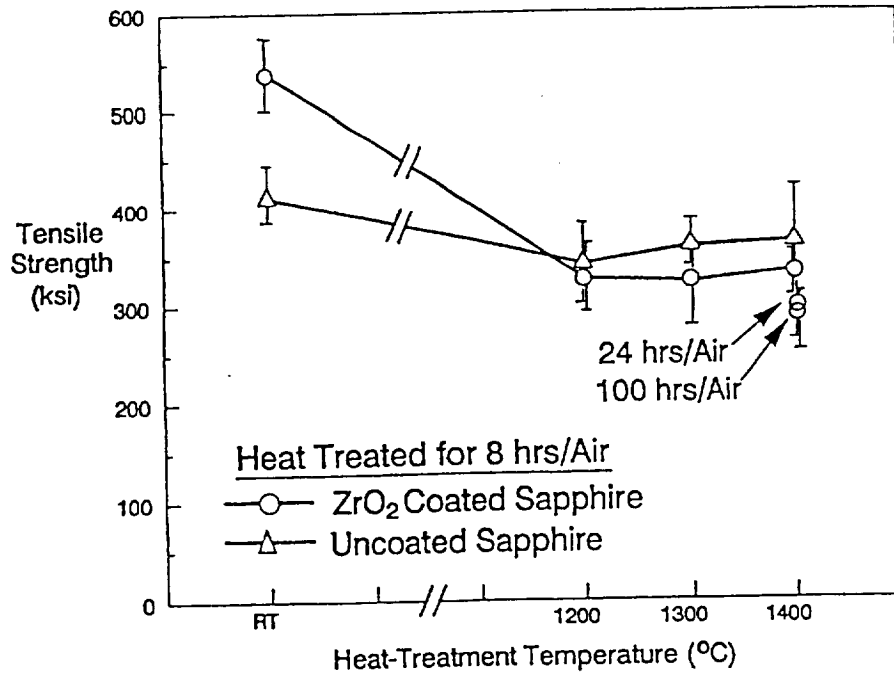
Figure 3. Effects of heat-treatment and ZrO_2 coatings on fiber tensile strengths.
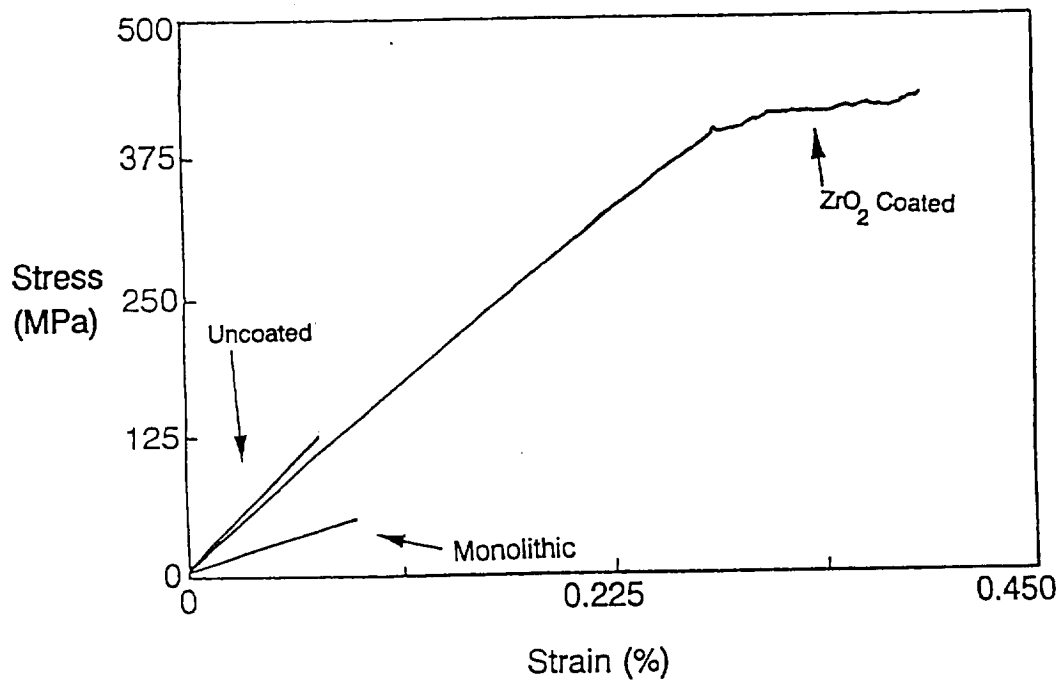
Figure 4. Stress vs. strain curves generated during tensile tests of monolithic Al_2O_3, ZrO_2 coated and uncoated sapphire reinforced composites.
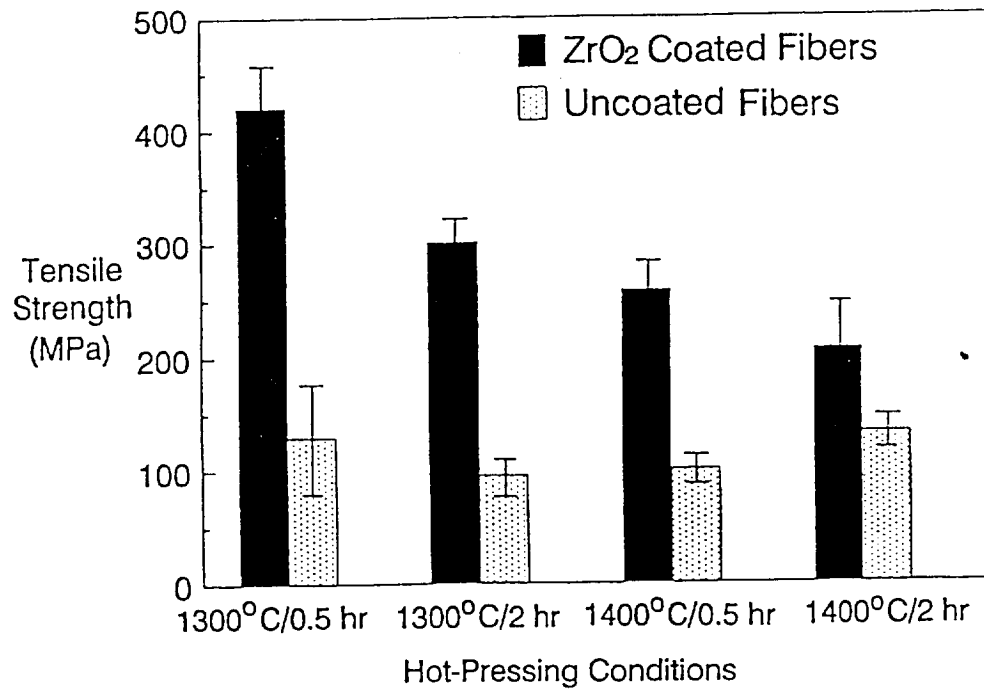
Figure 5. Effects of composite processing conditions and fiber coatings on ultimate composite tensile strengths.
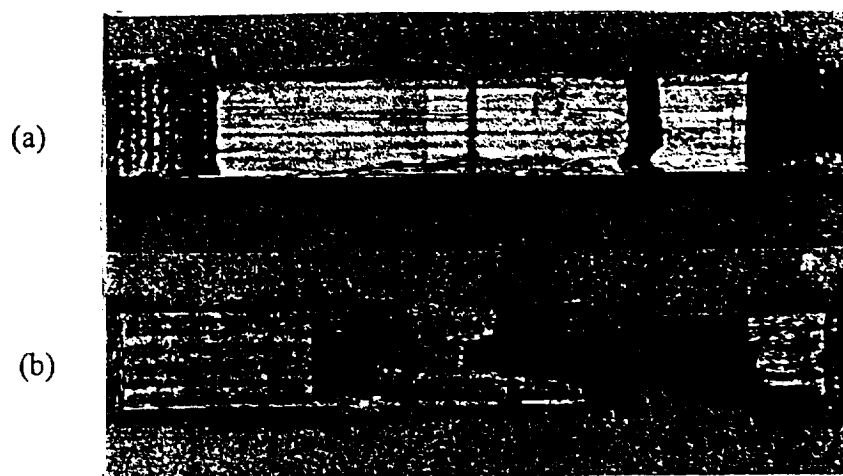
Figure 6. Composite tensile fracture samples with coated or uncoated fibers. (a)Uncoated fibers, (b)Coated fibers.
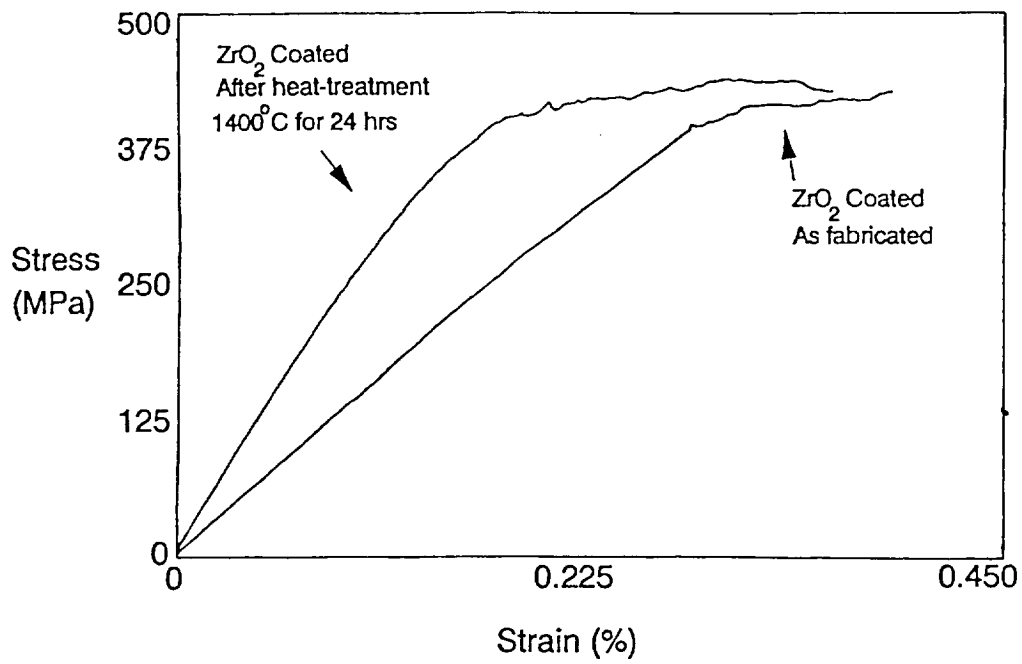
Figure 7. Stress vs. strain behavior for ZrO_2 coated fiber reinforced composites before and after heat-treatment.
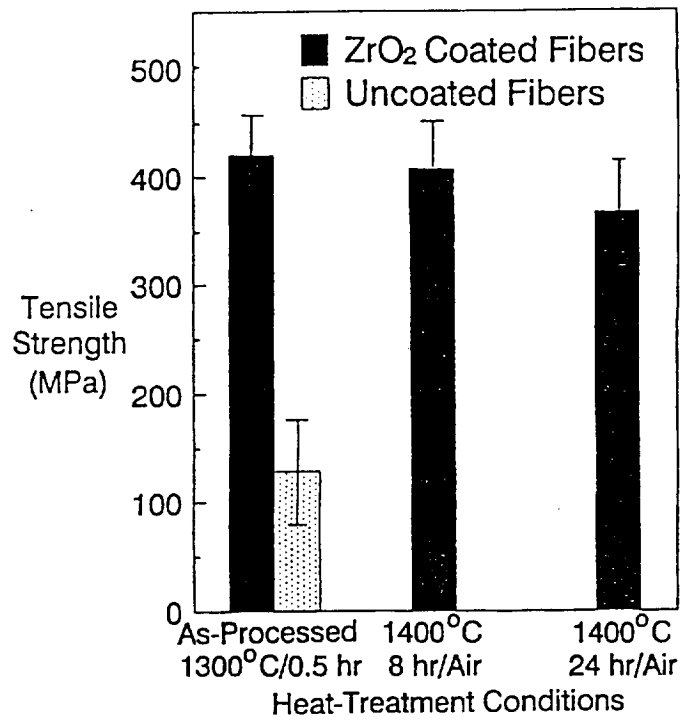
Figure 8. Ultimate composite tensile strengths after heat-treatment.

(a)

(b)
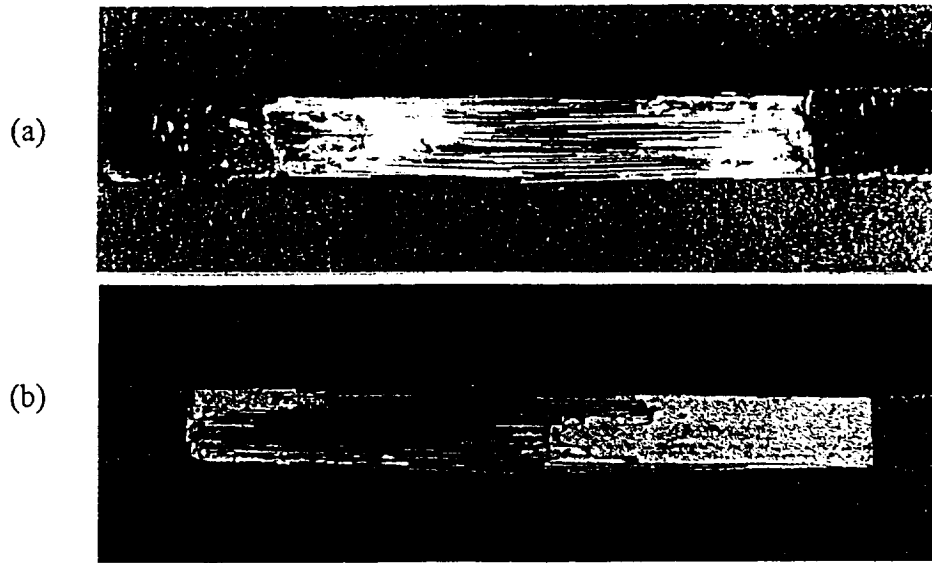
Figure 9. Coated fiber composite fracture samples after heat-treatment to 1400°C for (a) 8 hours or (b) 24 hours.
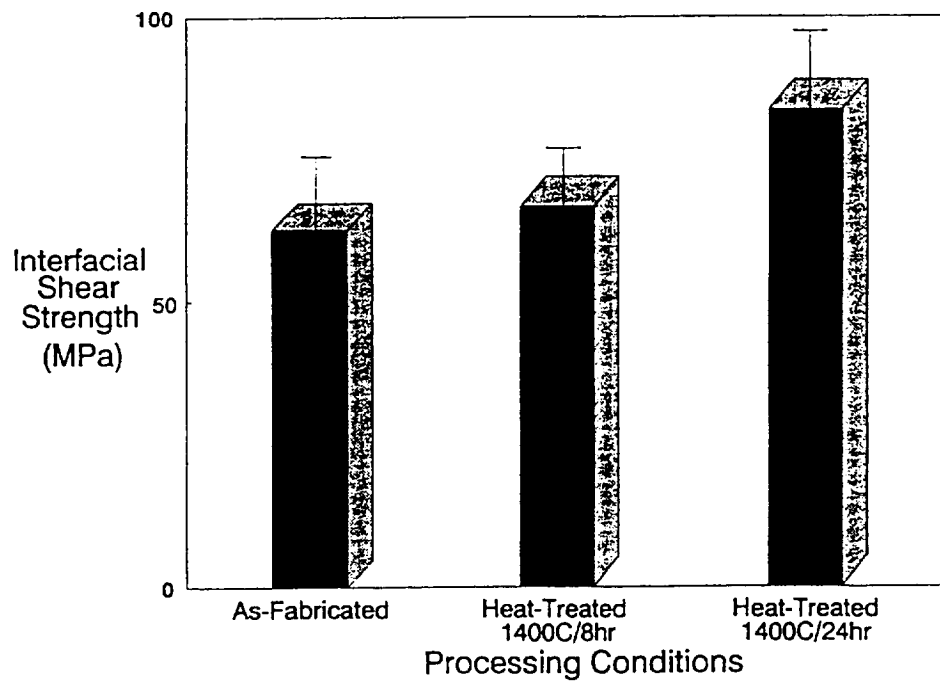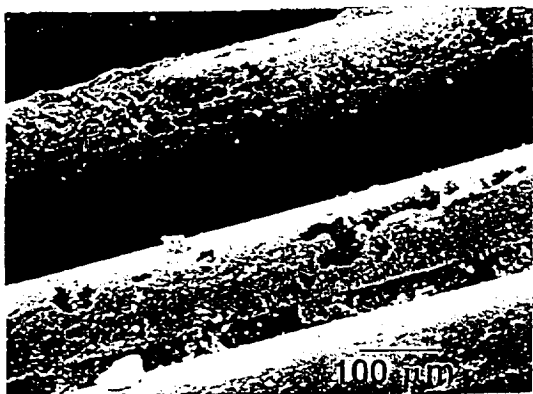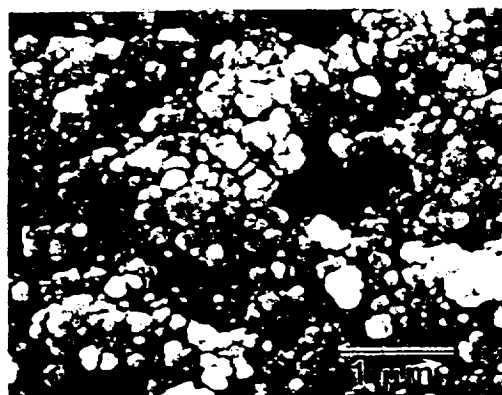

Figure 10. Effects of heat-treatment on the interfacial shear stress of ZrO_2 coated fiber reinforced composites.
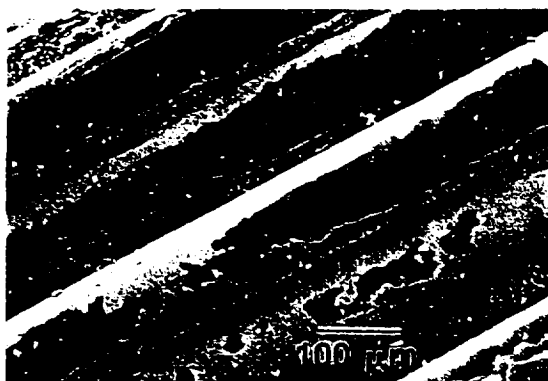
Fiber pull out from tensile test

Residual ZrO$_2$ on pulled out fiber

Figure 11. Micrographs of ZrO$_2$ coated fibers pulled out of the matrix during composite tensile test. Composite was hot-pressed 1300°C for 0.5 hours.

Fiber pull out from tensile test

Residual ZrO$_2$ on pulled out fiber

Figure 12. Micrographs of ZrO$_2$ coated fibers pulled out of the matrix during composite tensile test. Composite was originally hot-pressed at 1300°C for 0.5 hours then heat-treated at 1400°C for 24 hours.